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(54) IMPROVEMENTS IN OR RELATING TO FIRE RETARDANT COMPOSITIONS

- (71) We, CHEMISCHE WERKE ALBERT, a German Body Corporate, of Wiesbaden-Biebrich, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The invention relates to fire-retardant compositions which form a heat-insulating foam in the presence of fire, and are thus of use in rendering structures resistant to the effects of fire.
- Load-carrying structural members should not lose their stability and load-bearing capacity under the designed stress during a fire. In order to meet this requirement, steel girders for example, which are to be considered non-combustible as such, should not be heated above certain temperatures by the fire since otherwise the danger of buckling exists and they will thus contribute to the damage of a building or part of a building by fire. To prevent or retard this buckling as long as possible, it is specified in many cases that the steel structural members of a building must be provided with a plaster coat of a certain thickness. Furthermore, brickwork, if it has to meet certain requirements of fire protection, must carry a plaster coat of considerable thickness. Such fire-retardant layers of plaster can obviously increase the weight of the structure to an undesirable extent.
- As an alternative to plaster, it has been proposed to produce fire-retardant compositions capable of forming a layer of foam. Such compositions comprise a mixture of a urea-dicyanodiamide-formaldehyde precondensate, ammonium salts of phosphoric acids, preferably of orthophosphoric acid, skeleton-forming substances such as carbohydrates, e.g. starch and dextrin and, if desired, further conventional additives.
- These fire-retardant compositions are not only used for making combustible building materials, e.g. wood and wood materials, difficultly combustible, but also for the coating of non-combustible structural parts, e.g. steel and ferro-concrete constructions to make them "fire-retardant" or "fireproof" in the sense of DIN 4102 (Fire behaviour of building materials and structural parts).
- Thermally resistant mineral powders or mineral fibres favourably influence the fire resistance of so called mineral coatings (plaster and plaster carriers). Mineral additives have also been proposed in foam-forming fire-retardant compositions for the coating of structural parts.
- It has also been proposed to produce fire-retardant adhesives which contain glass fibres. The addition of glass fibres only serves for the formation of a non-combustible strip. Such products are thus not of use for the same purposes as the foam-forming compositions.
- The known fire-retardant compositions capable of forming a layer of foam have indeed been well proved but for some conditions of use it was desirable to improve their action even further. A disadvantage resides, for example, in the fact that in the resulting layers produced, hereafter referred to as insulating layers, cracks are readily formed. These impair not only the appearance but also have the disadvantage that with an increasingly

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longer action of the fire on such a layer the cracks become constantly deeper, whereby the insulating action of the protecting layer is steadily reduced. If it is possible, however, to avoid the crack formation, the insulating action of the protecting layer remains preserved.

According to the invention there is provided a fire-retardant composition capable of forming foam in the presence of fire comprising an aqueous precondensate of urea and dicyandiamide with formaldehyde, an ammonium salt of a phosphoric acid preferably an ammonium salt of orthophosphoric acid, a skeleton-forming material, and a mixture of glass fibres and asbestos in an amount of 5 to 20% by weight of the total composition.

As compared to those fire-retardant compositions which contain only one of these mineral components, these mixtures have an improved fire-retardant effect and a low tendency for crack formation or incineration to occur in the foam formed. Moreover, as compared to some hitherto known compositions, the drying speed of the compositions is higher.

According to a preferred embodiment of the invention, the mineral mixture of glass fibres and asbestos in the fire-retardant compositions consists of 25 to 70, preferably 30 to 60 percent by weight of glass fibres, preferably glass wool, and 75 to 30, preferably 70 to 40 percent complementally by weight of asbestos, e.g. asbestos fibres or microasbestos but preferably in the form of asbestos flour. This ratio of the mineral fillers has proved to be particularly advantageous because these mixtures have an especially high heat-insulating action associated with an absence of cracks in the foam. In glass wool, the glass is present as fine undulated fibres which are extensively felted with one another and are especially suitable for the present purpose due to this felting. The asbestos flour, which does not have a fibrous but rather a leaf-shaped or flake structure, supports this effect in that it fills the remaining hollow spaces. Only the conjoint use of these two substances enables an optimum effect for the present purpose.

In addition to the above-mentioned mineral substances, additional mineral substances compatible with the fire-retardant compositions may be added, e.g. mineral powders or mineral fibres, the quantity added varying between 5 and 20% for example calculated on the weight of the total mineral fillers. Substances suitable for this purpose are e.g. silicates, trass flour, talc, ground shale, quartz powder, mica, pumice powder, mineral wool (rock wool), slag wool, and foundry wool. The proportion of these additional substances should not, however, amount to more than 20% by weight calculated on the total quantity of mineral fillers since otherwise the desired action does not take place.

According to one embodiment, the com-

positions also contain one or more flame-retardant inorganic salts, such as ammonium sulphate, ammonium chloride or, preferably, boric acid or alkali metal borates, including polyborates. When the ammonium salt or a phosphoric acid is an ammonium salt of orthophosphoric acid, the flame-retardant inorganic salt may comprise an ammonium pyro- or polyphosphate. Also flame-retardant chlorine- or bromine-containing organic compounds can be used together with or instead of the above-mentioned inorganic salts, e.g. hexachloroethane or tris (dibromopropyl) phosphate. The skeleton-forming substances are suitably non-resinous substances rich in carbon, e.g. dextrin, starch, sugar or proteinaceous substances.

As further conventional additives there may be mentioned e.g. a) flowing agents, such as polyvinyl compounds, e.g. polyvinylacetate, or acrylic resins b) thixotropic substances such as amorphous silica, bentonite or thixotropic clay, c) fungicidal additives, such as sodium pentachlorophenate or organo-tin compounds, d) pigments or other water-insoluble materials, such as iron oxides, ammonium, alkaline earth and heavy metal phosphates, zirconium or lead compounds and e) anti-frothing compounds, e.g. polyglycol compounds.

The fire-retardant compositions according to the invention are particularly suitable for the coating of structural parts, sawn and round timber, chipwood and plywood sheets or articles made therefrom, e.g. ceilings and walls, and particularly for coating articles of steel and ferro-concrete constructions such as stays, girders, beams and panels. Very often the compositions are applied as a coating having a thickness of 600–800 μ .

In order that the invention may be better understood, the following examples are given by way of illustration only. Examples A to L illustrate fire-retardant compositions of known type, or those falling outside the scope of the invention, while Examples 1 to 6 illustrate compositions according to the invention. Percentages and ratios are by weight.

EXAMPLES 1 to 4 and comparison examples A to L

An aqueous precondensate prepared from 9 g. of urea, 15.9 g. of dicyanodiamide, 39.6 g. of an aqueous formaldehyde solution (30%, corresponding to 11.9 g. of formaldehyde) and 24.4 g. of monoammonium phosphate is mixed with 6 g. of dextrin and 3 g. of an aqueous dispersion (60% solids content) of 50% polyvinyl acetate and 10% tris (β,β,β -trichloroethyl) phosphate. The mineral substances or the mixtures thereof, given in the following Table, are introduced into this mixture.

For test purposes, first an undercoat comprising a non-plasticised and butanol-etherified phenol resol resin modified with urea, a highly acetalised polyvinyl butyral and zinc chromate, in solvents, such as benzene derivatives, e.g.

xylene, or glycol derivatives, e.g. ethylene glycolmonoethyl or-butyl ethers is applied to steel sheets in a thickness of 50 to 60 μ , i.e. at a rate of 300 g/m². The fire retardant composition is then applied to this undercoat in a layer thickness of 600 to 650 μ .

The testing of the fire-retardant compositions was carried out in a combustion chamber similarly to the specification of DIN 4102, but with steel sheets or steel plates instead of steel girders. The rear wall temperature was measured at intervals on the side not exposed to the standard fire. The condition of the foam formed was observed for 30 minutes.

In the following Table, the results of experiments with various compositions are summarised. For comparison the compositions A and B are given; these contain no mineral additives. Composition A was applied in a thickness of 750 to 800 μ or an application rate of 1500 g/m², and composition B in a thickness of 600 to 650 μ or application rate of 1000 g/m². The comparison of the temperatures observed with these compositions shows that a layer thickness of 750 to 800 μ is considerably more effective than one of 600 to 650 μ . With a layer thickness of 600 to 650 μ , the thickness of the fully foamed insulating layer was about 4 cm and with a layer thickness of 750 to 800 μ , about 5.5 to 6 cm.

The compositions C to L are given for further comparison and were used in a layer thickness of 600 to 650 μ , corresponding to an application rate of 1000 g/m². These compositions have a content of mineral materials which is outside the scope of the present invention. Composition H shows indeed the combination of glass wool and asbestos flour, but the proportion of mineral wool is considerably higher than is provided according to the invention. Compositions C to L show further

that glass wool and asbestos flour alone do not show the desired effect, not even together with other mineral fillers.

Compositions 1 to 4 are composed according to the invention; they show a superiority in the tests relative to the comparison compositions as regards the insulating action apparent from the temperature of the rear wall of the steel plate after a fire resistance period of 30 minutes, the temperature rise between the 5th and 30th minute, and the state of the foam after the 30th minute of the test, particularly as regards incineration, crack formation, adhesion and foam structure.

EXAMPLE 5

A fire-retardant composition was prepared from 41 g. of 30% formaldehyde solution, 12.5 g. of paraformaldehyde, 18 g. of monoammonium phosphate, 11 g. of dicyanodiamide, 16 g. of urea, 5.2 g. of dextrin and 1.2 g. of boric acid. 12% of a mixture of asbestos flour and glass wool in the ratio 1:1 were added to this mixture. The composition thus prepared shows as good an insulating action and foam properties as the other compositions 1 to 4 according to the invention.

EXAMPLE 6

An aqueous fire-retardant of the following composition was prepared: 40.2 g. of 30% formaldehyde (corresponding to 12.1 g. of formaldehyde), 15.2 g. of dicyanodiamide, 8.8 g. of urea, 23.0 g. of monoammonium phosphate, 10.0 g. of dextrin and 5 g. of water-soluble acid-curable phenol resol resin as binding agent. 6 g. of glass wool and 8 g. of asbestos flour were added to this mixture. The composition thus prepared shows as good an insulating action and foam properties as the other compositions 1 to 4 according to the invention.

THERMAL BEHAVIOUR OF FIRE-RETARDANT COMPOSITIONS COATED ON STEEL PLATES

Composition No.	Nature and proportion of mineral additives in % by weight (on total mixture)	Steel rear wall temp. after 30 minutes °C	Temperature increase from the 5th to the 30th minute, °C	Adhesion of the foam	Change of the foam in the test period of 30 minutes
For comparison:					
A) (1500 g/m ² coating weight)	—	245/255	115/125	good	start of incineration after 12 minutes of test, crack formation after 17 minutes of test
B) (1000 g/m ² coating weight)	—	315	175	good	start of incineration after 10 minutes test, crack formation after 17 minutes of test
C)	9.5 glass wool	265	165	good	start of incineration after 21 minutes of test, no crack formation
D)	15.0 glass wool	355	225	good	no incineration or crack formation
E)	8.5 glass wool 6.3 ground mica	290	160	good	no incineration or crack formation
F)	8.5 glass wool 6.3 expanded mica (Vermiculite)	320	175	bad exfoliation after 27 minutes of test	no incineration, crack formation after 20 minutes of test
G)	6.5 glass wool 8.5 kieselguhr	310	170	good	no incineration, crack formation after 22 minutes of test
H)	7.5 glass wool 6.0 mineral wool 6.5 asbestos flour	330	225	good	no incineration, crack formation after 23 minutes of test

Composition No.	Nature and proportion of mineral additives in % by weight (on total mixture)	Steel rear wall temp. after 30 minutes °C.	Temperature increase from the 5th to the 30th minute, °C.	Adhesion of the foam	Change of the foam in the test period of 30 minutes
For comparison:					
I)	7.5 glass wool 8.5 mineral wool	350	250	bad exfoliation after 28 minutes of test	no incineration, crack formation after 20 minutes of test
K)	2.0 asbestos flour 2.0 mineral wool	240	150	bad exfoliation after 25 minutes of test	incineration after 18 minutes of test, crack formation after 19 minutes of test
L)	11.5 asbestos flour	235	115	good	no incineration, crack formation after 27 minutes of test
According to the invention:					
1)	5.5 glass wool 6.0 asbestos flour	220	105	good	no incineration or crack formation
2)	7.0 asbestos flour 4.0 glass wool	220	100	good	no incineration or crack formation
3)	7.5 asbestos flour 4.0 glass wool	185	85	good	no incineration or crack formation
4)	7.5 asbestos flour 7.5 glass wool	225	125	good	no incineration or crack formation

WHAT WE CLAIM IS:—

1. A fire-retardant composition capable of forming foam in the presence of fire comprising an aqueous precondensate of urea and dicyandiamide with formaldehyde, an ammonium salt of a phosphoric acid, a skeleton-forming material, and a mixture of glass fibres and asbestos in an amount of 5 to 20% by weight of the total composition.
2. A composition as claimed in claim 1, in which the glass fibres and the asbestos are present in a ratio of 25 to 70% by weight of glass fibres to 75 to 30% complementally by weight of asbestos.
3. A composition as claimed in claim 2, in which said ratio is from 30 to 60% by weight of glass fibres to 70 to 40% complementally by weight of asbestos.
4. A composition as claimed in any one of the preceding claims, in which the glass fibre is present in the form of glass wool.
5. A composition as claimed in any one of the preceding claims, in which the asbestos is present in the form of asbestos flour.
6. A composition as claimed in any one of the preceding claims, in which the ammonium salt of a phosphoric acid is an ammonium salt of ortho-phosphoric acid.
7. A composition as claimed in any one of the preceding claims including one or more additional fire-retardant inorganic salts.
8. A composition as claimed in claim 7 in which said additional salts are ammonium sulphate or chloride, or boric acid or an alkali metal borate or polyborate or, when the ammonium salt of a phosphoric acid is an ammonium salt of orthophosphoric acid, said additional salt comprises an ammonium pyro- or polyphosphate.
9. A composition as claimed in any one of the preceding claims including a flame-retardant organic compound containing chlorine and/or bromine.
10. A composition as claimed in claim 9 in which said organic compound is hexachloroethane or tris(dibromopropyl) phosphate.
11. A composition as claimed in any one of the preceding claims in which said skeleton-forming material is a dextrin, starch, sugar or protein.
12. A composition as claimed in any one of the preceding claims, in which a further mineral filler is present in an amount of not more than 20 weight %, calculated on the total amount of the mineral fillers.
13. A composition as claimed in claim 12 in which said further filler is a silicate, trass flour, talc, ground shale, quartz powder, mica, pumice powder, mineral wool, slag wool or foundry wool.
14. A composition as claimed in claim 12 or claim 13 in which said further filler forms from 5 to 20 weight % of the mineral fillers.
15. A composition as claimed in any one of the preceding claims, including a water soluble acid-curable phenol resol resin as binding agent.
16. A composition as claimed in any one of the preceding claims, which includes one or more other conventional additives as hereinbefore set forth.
17. A composition as claimed in claim 16 including a flowing agent, a thixotropic substance, a fungicide, a pigment or a froth-reducing additive.
18. A fire-retardant composition as claimed in claim 1 substantially as described herein.
19. A fire-retardant composition as claimed in claim 1 substantially as described herein with reference to any of examples 1 to 6.
20. A fire-resistant article which has been at least partly coated with a composition as claimed in any one of the preceding claims.
21. An article as claimed in claim 20 on which said coating has a thickness of 600—800 μ .

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